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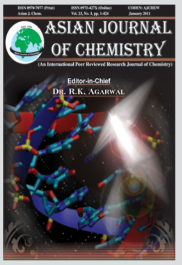

Measurement and Correlation of Solubility of Sodium Sulfide in Water and Several Organic Solvents Plus Water

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The solubility of sodium sulfide in water and several organic solvents plus water had been determined by the synthetic method. The experimental data were correlated with the modified Apelblat equation. The experimental data of solubility of sodium sulfide were in perfect accord with the data calculated by the equation.

Key Words: Measurement and correlation of solubility, Sodium sulfide, Apelblat equation.

INTRODUCTION

The study of phase equilibria in salt-containing systems is very important for many industrial applications. More particularly, a knowledge of accurate solubility is needed for the design of separation processes such as extractive crystallization[1] or for the safe operation of different processing units such as distillation columns, absorption units and extraction plants[2]. They can also supply basic and theoretical data to industrial production[3].

Sodium sulfide is an important nucleophile and reducing agent derived from H_2S. It can be used for the synthesis of thiols, thioethers and disulfides[4] and reduces aromatic nitro compounds to amines as a reducing agent. In present studies, we used sodium sulfide for the synthesis of di-*sec*-butyl disulfide. It is found that the solubility of sodium sulfide extremely important for the optimal conditions. Normally methanol, ethanol, N,N-dimethylformamide, dimethyl sulfoxide or 1,4-dioxane plus water as solvents have been in this sort of reaction in the literature[5-8]. But only a few solubility data of sodium sulfide data have been reported and no solubility data of sodium sulfide in these mixed solvents have been reported so far. Therefore in this work, the solubility of sodium sulfide in the solvent above was measured. The experimental data were correlated with the modified Apelblat equation and the solubility correlated by models agreed with the experimental data to within ± 1.6 %.

EXPERIMENTAL

In all experiments, distilled deionized water was used. Sodium sulfide, methanol, ethanol, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and 1,4-dioxane were supplied by Tianjin Kermel Chemical Reagent Co. and were of AR grade with a purity higher than 99.5 %.

The solubility of sodium sulfide in different solvents was measured by the synthetic method. The laser monitoring observation technique was used to determine the dissolution temperature of the solid-liquid mixture of known composition. The laser monitoring system consists of a laser generator, a photoelectric transformer and a light intensity display.

The experiments were carried out in a 50 mL jacketed glass vessel with a magnetic stirrer, a constant temperature (± 0.02 K) was maintained at the required temperature by circulating water through the outer jacket from a thermoelectric controller. A glass bushing with a mercury glass micro-thermometer was inserted into the inner chamber of the vessels for the measurement of the temperature[9,10].

Predetermined amounts of sodium sulfide and the solvents for the solubility measurement were weighed by an electronic balance (Mettler Toledo AB204-N) with an accuracy of ± 0.0001 g and then transferred into the vessel. The contents of the vessel were heated very slowly at the rate of 1 K/h until the system reached balance. In the early stage, the laser beam was blocked by the particles of sodium sulfide unsolved. The intensity of the laser beam increased gradually along with the increase of sodium sulfide dissolved. The intensity of the laser beam reached maximum when the last portion of sodium sulfide just disappeared. The temperature was recorded. The solubility of sodium sulfide was expressed by mole fraction with the formula as follows[10]: Where m_1 represents the mass of solute; m_2 and m_3 represent the mass of solvents, respectively.

M_1 is the molecular mass of solute; M_2 and M_3 are the molecular mass of solvents correspondingly.

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \quad (1)$$

where m_1 represents the mass of solute; m_2 and m_3 represent the mass of solvents, respectively. M_1 is the molecular mass of solute; M_2 and M_3 are the molecular mass of solvents correspondingly.

RESULTS AND DISCUSSION

Before doing the experiment, confirmation of the accuracy about the apparatus and method was done by comparing our solubility data of sodium chloride in water with those in literature. The results were listed in Table-1. The table showed that the measurement agreed with the data in the literature with a mean relative deviation of 0.20 %.

TABLE-1
SOLUBILITY OF SODIUM CHLORIDE IN WATER

NaCl + H_2O				
T (K)	293.15	203.15	213.15	233.15
x	0.0998	0.1002	0.1012	0.1028
x (lit.)[11]	0.0996	0.1001	0.1009	0.1026
RD	0.0020	0.0010	0.0030	0.0019

The solubility data of sodium sulfide in water and organic solvents plus water at different temperatures were presented in Tables 2 and 3. The temperature dependence of sodium sulfide in solvents is described by the modified Apelblat equation:

$$\ln x = A + \frac{B}{T} + C \ln T \quad (2)$$

where x = mole fraction of solubility of sodium sulfide. T = absolute temperature. A, B and C are the model parameters.

TABLE-2
SOLUBILITY OF Na_2S IN WATER AND FIVE ORGANIC SOLVENTS PLUS WATER WITH THE w = 0.20

T (K)	x	100RD	T (K)	x	100RD
Water					
289.95	0.04515	2.180	301.65	0.05780	-1.583
293.40	0.04785	-0.319	302.95	0.06112	0.805
296.85	0.05164	-1.096	305.35	0.06449	0.254
299.40	0.05507	-0.892	307.25	0.06793	0.736
Methanol + water					
289.65	0.04402	0.813	299.05	0.05456	-0.211
290.95	0.04500	-0.081	301.40	0.05724	-1.054
293.95	0.04806	-0.696	302.45	0.05950	0.302
296.25	0.05130	0.320	304.35	0.06246	0.606
Ethanol + water					
290.65	0.04258	3.761	303.05	0.05580	-0.591
294.30	0.04478	-0.338	306.65	0.06179	0.376
296.25	0.04592	-2.799	309.35	0.06585	-0.188
300.55	0.05222	-0.856	311.05	0.06948	0.798
DMF + water					
296.20	0.05423	0.182	300.95	0.06024	0.380
297.05	0.05507	-0.167	302.25	0.06177	0.153
298.75	0.05699	-0.464	303.75	0.06342	-0.321
299.75	0.05861	0.181	304.75	0.06497	0.045
DMSO + water					
288.75	0.03858	1.149	300.55	0.05316	0.161
291.15	0.04082	0.058	302.55	0.05644	0.580
294.15	0.04379	-1.324	304.95	0.05977	-0.363
296.05	0.04683	0.069	308.75	0.06677	0.162
298.55	0.04997	-0.435	–	–	–
1,4-Dioxane + water					
292.55	0.04441	-0.143	298.60	0.05230	0.034
294.55	0.04702	0.207	299.45	0.05333	-0.281
295.75	0.04844	-0.022	300.45	0.05495	0.055
297.00	0.05013	0.062	301.55	0.05660	0.078

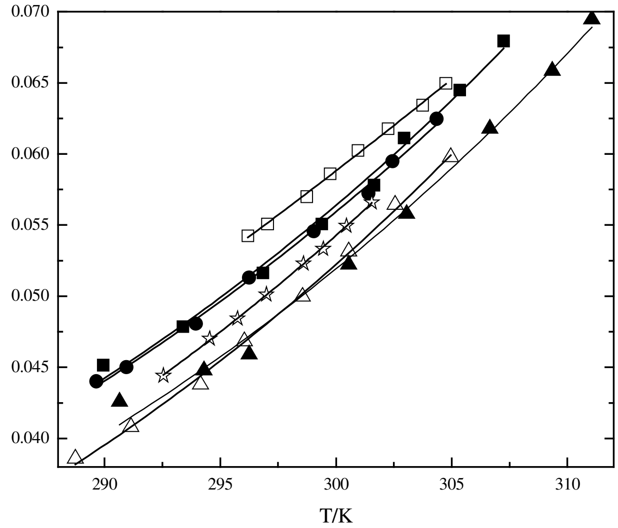

Fig. 1. Solubility curves of sodium sulfide in water and organic solvents + water: ■, water; ●, methanol + water; ▲, ethanol + water; □, DMF + water; △, DMSO + water; ☆, 1,4-dioxane + water

The solubility curves by eqn. 2 are shown Fig. 1. The values of parameters A, B, C and the root-mean-square deviation:

$$\text{RMSD} = \left[\frac{1}{N-1}\sum_{i=1}^{N}(x_{ci} - x_i)^2\right]^{1/2} \quad (3)$$

where N = number of experimental points, x_{ci} represents the solubilities calculated from eqn. 2 and x_i represents the experimental solubility values. The relative deviations between the experimental value and calculated value are also listed in Table-2 (where w = initial mass fraction of the organic solvent to the total solvent, equal to 0.20). Relative deviations (RD) are calculated according to:

$$\text{RD} = \frac{x - x_c}{x} \quad (4)$$

The relative average deviations (RAD) and the root-mean-square deviation (RMSD) by eqn. 2 are listed in Table-3. The RAD is defined as

$$\text{RAD} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{x_i - x_{ci}}{x_i}\right| \quad (5)$$

From Table-3, it can be found that the calculated solubility data show good agreement with the experimental data. The relative deviations by eqn. 2 among all of these values do not exceed 1.6 %, which indicates that the modified Apelblat equation is suitable to correlate the solubility data of sodium sulfide in the selected solvent systems.

TABLE-3
MODELING PARAMETERS AND CORRELATION COEFFICIENT OF SODIUM SULFIDE IN DIFFERENT SOLVENTS BY EQN. 2

Solvent	A	B	C	R^2	10^3 RMSD	10^2 RAD
Water	-119.47	3339.47	18.49	0.9935	0.64	0.98
Methanol + water	-93.19	2207.08	14.54	0.9975	0.34	0.51
Ethanol + water	-115.49	3084.76	17.93	0.9932	0.84	1.21
DMF + water	57.06	-4318.29	-7.98	0.9981	0.17	0.24
DMSO + water	-94.95	1979.78	14.97	0.9989	0.31	0.48
1,4-Dioxane + water	-81.83	1493.93	12.96	0.9997	0.08	0.11

*R^2 is correlation coefficient.

The graph of solubility of sodium sulfide in the selected solvent systems is shown in Fig. 1. It can be observed from the figure that all of the solubility follows the tendency that the solubility increases as the temperature rises. The solubility of sodium sulfide in water is greater than that in the selected solvents except in DMF plus water. The addition of DMF increases the solubility of sodium sulfide while the addition of methanol, ethanol, DMSO and 1,4-dioxane lower it. Methanol lowers it more than ethanol, which is in accord with the physical property of sodium sulfide. The solubility of sodium sulfide in DMSO + water (w = 0.20) is greater than that in ethanol + water (w = 0.20). It can be observed from Fig. 1 that the solubility in selected solvents follow the order DMF + water > water > methanol + water > 1,4-dioxane + water > DMSO + water > ethanol + water on the whole.

Conclusion

The solubility of sodium sulfide in the selected solvent systems has been measured by a dependable experimental method and simple solubility apparatus. The modified Apelblat equation based on solid-liquid phase equilibrium principles is used to correlate the solubility data of sodium sulfide in the selected solvent systems, the relative deviation among all these values does not exceed 1.6 %, the solubilities calculated by the model show good agreement with the experimental data. The experimental solubility in this work can be used as essential data and as a basis for selecting the operation conditions.

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